ON THE THEORY OF ELECTRON, H-ATOM AND PROTON TRANSFERS

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The initial part of this article discusses some recent experiments on electron transfer reactions and comments on the related theory, including the frequency of solvent fluctuations. Also described are recent advances with Babamov and Lopex on the dynamics of H-atom transfer reactions. We then outline the application of the basic idea to H and H^+ transfers in complex systems and in condensed phases (fast H-coordinates, slow remaining coordinates). Similarities and differences between electron transfers and H or H^+ transfers are next described. The relation of the present theory of such transfers to conventional transition state theory is discussed.

I. Outline

There have been a number of recent results for electron transfer reactions (described in Sec. II) and a recent development in the theory of light atom transfer (e. g., H, D) reactions by Babamov and Lopez in our group (described in Sec. III) for collinear systems such as I + HI → IH + I. The latter theory is based on a "Born-Oppenheimer" separation in which the I's are the slow particles and H the fast ones. We then indicate in Sec. III how this concept is extended to more complicated processes, such as those occurring in condensed phases. We also note the breakdown of simple Franck-Condon calculations when applied to atom transfers. In Sec. IV some similarities and differences in the transfer of electrons between reactants, as compared with the transfer of light nuclei such as H and H^+, are described. The relation of the theory of all three to conventional transition state theory is discussed.

II. Recent Developments in Electron Transfers

This part of the paper discusses some recent work in this field. The topics we consider are

1. electronic matrix elements in electron transfers; nonadiabaticity vs adiabaticity;
2. absolute rate calculations of electron transfer rate constants;
3. solvent effects, both when solvent relaxation is rate controlling and when it is not; an expression for the rate of formation of solvent fluctuations for facilitating electron transfer is given;
4. comparison of heterogeneous (electrochemical) and homogeneous rate constants;
5. distance effect on electron transfer rates; and
6. other aspects including orbital and orientation effect on electron transfer rates (preliminary calculations), photoelectric emission experiments, and application of the quadratic free energy expression to the other classes of reactions.

1. Electron Transfer Matrix Elements

Second order bimolecular rate constants k_{bi} have been expressed in terms of first order constants k(R) at a reactants' separation distance R by integrating over all R using the pair distribution function g(R), e. g., refs. (1-4):

$$k_{bi} = \int_0^\infty k(R)g(R)\,4\pi R^2\,dR \qquad (1)$$

g(R) can be expressed in terms of some "work" term $w_r(R)$ to bring

the reactants r to a separation distance R:

$$g(r) = \exp[-w_r(R)/kT] \quad . \tag{2}$$

Equation (1) is an approximation which tacitly assumes (4, 5) that R itself is not the reaction coordinate. With this approximation eq. (1) can be deduced from Ref. (5).

A first order nonadiabatic electron transfer rate constant $k_{na}(R)$ has been written in the form (1, 6)

$$k_{na}(R) = \frac{2\pi}{\hbar} |H_{12}|^2 \sum_{i,f} P_{f \leftarrow i} p_i^{eq} \delta(E_f - E_i) \tag{3}$$

where $P_{f \leftarrow i}$ is the Franck-Condon overlap factor $|\langle \psi_f | \psi_i \rangle|^2$ of the wavefunctions for nuclear motion of reactants and solvent (in state i) and of products and solvents (in state f), p_i^{eq} is the Boltzmann distribution function for finding the system in the i'th initial state of the entire system containing the reactants, and the Dirac delta function $\delta(E_f - E_i)$ ensures that there is conservation of energy during the electron transfer act. Because of the 'continuum' of final states f, the summation over f becomes an integral and the delta function disappears on integration.

We note that the maximum value that the double sum in eq. (3) can have is when there is extensive overlap of each ψ_i with a corresponding ψ_f (hence, no Franck-Condon barrier), so that for every i $P_{f \leftarrow i}$ is unity for some f. The double sum is then found to be (Appendix A), approximately $1/\hbar\omega$, where $\omega/2\pi$ is a typical relevant vibration frequency. Thus,

$$k_{na}^{max}(R) \cong \frac{2\pi}{\hbar} |H_{12}|^2 \frac{1}{\hbar\omega} \quad . \tag{4}$$

If k_{na}^{max} exceeds 10^{13} s^{-1} the nonadiabatic approximation (and hence eq. 4) breaks down, and the reaction is adiabatic under such conditions of no Franck-Condon barrier.

Some recent calculations of H_{12} for the $Fe(H_2O)_6^{2+,3+}$ reaction have been reported by Newton and co-workers (3, 7, 8). Previously, in calculations on this reaction a value of H_{12} of 2.7 cm^{-1} at R = 7.3 Å had been obtained, but a later calculation showed that for a more elaborate wavefunction H_{12} at 7.3 Å was 9 cm^{-1}, while with a more favorable geometry for overlap it became 26 cm^{-1} (8). The r_{max} which maximized the integrand in eq. (1) was roughly 5.3 Å, and here the full calculation gave $H_{12} \sim 120$ to 130 cm^{-1} (8). An H_{12} of only ~ 60 cm^{-1} would have been sufficient to make k_{na}^{max} reach the adiabatic value ($\sim 10^{13}$ s^{-1}) had there been no Franck-Condon barrier. However,

the actual reaction is not quite adiabatic: adiabaticity also depends on the slopes of the reactants' and products' potential energy curves for the prevailing Franck-Condon barrier (7). (Cf. Landau-Zener theory for curve crossing problems.) The net result is that the reaction deviates from adiabaticity, in these available calculations, by a factor of about 1/5 (7). An important feature of attaining a substantial H_{12} in such calculations was the mutual penetration of the two aquo ions (i.e., $r \equiv 5.3$ Å) or a suitable orientation. (However, the H_{12}'s may be inaccurate, because of the sensitivity of the tails of the wavefunctions to approximations.)

For reactants such as ruthenium bipyridyls or iron phenanthrolines, even some delocalization of the electron of the metal cation over the aromatic rings is expected to lead to a substantial H_{12}. Indeed, reactions of these compounds with other reactants, when accompanied by large negative $\Delta G^{0\prime}$s are diffusion-controlled, and so can't be far from adiabatic: If they were highly nonadiabatic they could never be diffusion-controlled.

2. Absolute Rate Calculations

The factors which influence the reaction rate constant include (i) the changes, as a result of electron transfer, within the innermost coordination shell of each reactant, (ii) the changes outside of this shell, (iii) the standard free energy of reaction (which is zero for self-exchange reactions), (iv) the frequency of "collisions", and (v) the electronic matrix element, when the reaction is predominantly nonadiabatic. The 'collision frequency' includes, in the electron transfer case, the range of R's over which electron transfer can occur significantly (more precisely which contribute to the integral in eq. (1) (4)). We comment in Appendix B on the first factor.

Recently, there have been determinations of the metal-ligand bond lengths of electron transfer reactants in solution using EXAFS. This technique not only extends the X-ray data from the solid state to solutions but also increases considerably the number of systems for which the bond length changes Δq^0 are known. An extensive table is given by Brunschwig et al. (9). For a number of systems Δq^0 is very small: $Fe(CN)_6^{3-,4-}$ (0.01 Å), $Fe(phen)_3^{2+,3+}$ (0.00), $Co(bpy)_3^{2+,3+}$ (-0.02), $Ru(NH_3)_6^{2+,3+}$ (0.03). For such systems, the contribution of the innermost coordination shell to the reorganization energy is very small indeed, and is dominated by the solvent contribution from outside that shell. For a number of other systems, there is a substantial Δq^0, and then the innermost coordination shell is a major contributor to the reaction barrier: $Fe(H_2O)_6^{2+,3+}$ (0.13), $Co(NH_3)_6^{2+,3+}$ (0.22), $Co(phen)_3^{2+,3+}$ (0.19), and $Cr(H_2O)_6^{2+,3+}$ (0.32 for five ligands and 0.09 for one) (9). Nuclear tunneling factors usually contribute only between a factor of 1 to 7 in the self-exchange rate constants (10, 11). The results for the absolute rates, obtained with expressions which are substantially the same as those which we gave earlier (5, 12), yielded reasonable agreement with the experimental rate constants (13), considering that an error in the calculated free energy of

activation of 1.4 kcal mol^{-1} yields an error of a factor of ten in the rate constant. Adiabaticity was assumed.

Although we have considered the rate constants themselves in this section, the most widely used application of the electron transfer theory we've described continues to be the 'cross-relation' (14),

$$k_{12} \sim (k_{11}k_{22}k_{12}f_{12})^{\frac{1}{2}} \qquad (5)$$

relating the rate constants of cross-reactions to those of self-exchange reactions. A sampling of recent tests is given elsewhere (15). Tests involving cross reactions of inorganic reagents with cytochrome c was given by Sutin (16).

3. Solvent Effects

Several systems have been studied in which the $1/D_{op} - 1/D_s$ solvent effect (17) applies to electron transfer rate constants. These include the work on aromatic anions-aromatic molecules (18), bis-arene chromium $^{1+,0}$ reaction (19), the tris-hexafluoroacetylacetonato $Ru^{1+,2+}$ one (20), and various intervalence-transfer optical systems, e.g., (21-23). On the other hand, there was no correlation in the case of the ferrocene-ferrocenium $ion^{0,1+}$ reaction (24) or in the case of the spectrum of compound II below (23).

The solvent effect represented by $1/D_{op} - 1/D_s$ is nonspecific and would be expected to break down when (i) the electronic overlap is no longer weak, or (ii) the solvent enters the the inner coordination shell, if any, or (iii) there is a specific solvent effect. An example of (i) is found in the pyrazine bridge system (compound II below). Results on charge transfer spectra have been reported (23) for I and II:

I: $(NH_3)_5Ru^{III}$—N⟨⟩—⟨⟩N—$Ru(NH_3)_5^{II}$

II: $(NH_3)_5Ru^{III}$—N⟨⟩N—$Ru(NH_3)_5^{II}$.

The results for I showed the expected (25) theoretical dependence of spectral absorption maximum on $(1/D_{op} - 1/D_s)$, with a slope which agreed with the theoretical value (D_{op} and D_s are the optical and static dielectric constants). Compound II showed no dependence--reflecting a strong rather than weak electronic interaction of the two Ru's via the pyrazine bridge.

Kosower and Huppert recently studied solvent effects on fluorescence quenching when the latter was caused by intramolecular charge transfer (26). They considered an amino napthalenesulphonic acid derivative and a cyanodimethylamino benzene. In each case they found that the fluorescent lifetimes in a variety of solvents equaled the 'constant charge' longest dielectric relaxation time $\tau' = (D_{op}/D_s)\tau$ for each solvent, where τ is the usual ('constant field') relaxation time. For water, when $\tau \sim 8$ ps, $\tau' \sim 0.2$ ps. These results are striking in showing quite directly how experimental reaction rate constants can be related to bulk dielectric properties, in the present case when the reaction is 'barrierless'.

One can use this result to calculate the rate constant for formation of polarization fluctuations in a solvent: Suppose that τ' is the relaxation time in the sense of being the reciprocal of a rate constant (27) rather than being a 'half-life'. Let the fluctuation be such that its free energy of formation is ΔG^*. The relaxation time for decay of the fluctuation is $(D_{op}/D_s)\tau$, corresponding to a first order rate constant of $(D_s/D_{op}\tau)$. Thus, by microscopic reversibility the rate constant for forming the solvent fluctuation is

$$k = (D_s/D_{op}\tau)e^{-\Delta G^*/RT} \quad . \tag{6}$$

The value of ΔG^* for fluctuations in the solvent outside the innermost coordination shell has been given previously (17) in terms of $1/D_{op} - 1/D_s$. τ' has also been used in reaction rates for other types of reactions, e.g., (28).

4. Electrochemical Rate Constants

A recent survey of the comparison between homogeneous self-exchange rate constants k_{ex} and electrochemical rate constants k_{el} has been given by several authors (29, 30). The slope of the log k_{el} vs log k_{ex} is approximately $\frac{1}{2}$, as predicted for the case where the reactant center-reactant center distance in the homogeneous case is twice the reactant center-electrode surface distance (14). The very fast reactions showed enhanced deviations. The electrochemical rate constants in general tended to be somewhat slower than expected from the simple theory (roughly a factor of 10 in the region where the log-log plot had a slope of $\frac{1}{2}$). The reason may lie in a somewhat larger reactant-metal distance, resulting in a somewhat larger solvent reorganization energy and, possibly, in an extra nonadiabaticity.

The slope of the log k_{el} vs the activation overpotential plot has been determined for a number of organic reactants by Savéant and co-workers (31). The results show a curvature, as expected from theory.

5. Distance Effects in Electron Transfer Rates

At large separation distances the overlap of the electronic orbitals of the reactants becomes very small and the electronic H_{12} matrix element thereby also becomes small, varying roughly exponentially with separation distance R, and the reaction is now nonadiabatic. We have

$$k \propto e^{-\alpha R} \quad . \tag{7}$$

In frozen media the closer reactants react first and then the more distant ones. There results a peculiar kinetics for such second order reactions, the amount reacted now varying with log t (32-34). From such studies values of α have been estimated. For reactions between aromatic molecules and aromatic anions it is about 1.1 Å (33), and between pyrene$^+$ and tetramethylene phenylene diamine it is about 1.15 $Å^{-1}$ (34). Intramolecular electron transfer studies are desirable and are in progress in several laboratories on the effect of separation distance R on the rate.

We consider next a biological system, cytochrome c - cytochrome c peroxidase. A recent approximate estimate of the edge-to-edge distance between the hemes is about 16.5 Å (35). The rate constant for electron transfer is known to be at least as fast as 10^4 s^{-1} (36). The maximum k expected if α were 1.1 $Å^{-1}$ would be 10^{13} exp(-18.1), i.e., $\sim 10^5$ s^{-1}, which, thus far, is consistent with the above existing minimum value of k.

A solvational distance effect, expected from the solvent reorganization theory (17), has been used to interpret some experimental results (37).

6. Other Aspects

Recent interesting photoelectric emission experiments and interpretation have been performed by Delahay and his group (38). He has been able to interpret the results in terms of concepts closely related to those used for thermal electron transfers and described earlier: contributions from the inner coordination shell and from the solvent outside it.

One continuing interest has been the investigation of highly exothermic reactions and a possible 'inverted' effect on the rate. We have discussed recent results elsewhere (39). A detailed calculation was presented (40) for the highly exothermic reaction of electronically-excited $Ru(bipy_3^{2+}$ with various metal bipyridyls. The absence of any large inverted effect in these reactions was clarified in part. However, not included was the role, if any, of high frequency CH vibrations in accepting some of the excess energy of reaction by producing excited CH vibrational states, and thereby reducing the

effective $-\Delta G^0$ acting on the other coordinates. Indeed, it would be useful to repeat these and related experiments using deuterated systems, which would have less ability to accept the excess energy of reaction and so might show a larger tendency to 'inverted' behavior if CH vibrations play a role.

Orientational or geometrical effects on electron transfer rates are known. It may be recalled that in the electron transfer reaction between hexahelicene and its anion, the dℓ pair reacted four times more slowly than the dd pair, which itself was diffusion controlled (41). Orientational effects for spheroidal shaped molecules have been examined theoretically by Siders and Cave in our group using a simple model (constant potential energy inside the spheroid) which will be described elsewhere. Appropriate orientations produce a more favorable H_{12}. Larsson has discussed from a molecular orbital viewpoint orbital effects on electron transfer rates (42).

Reviews or adaptations of electron transfer theory to organic systems has been described by Eberson (43) and by Kochi (44). The quadratic relation between the free energy of activation and that of reaction, first obtained for electron transfer reactions (17), has now been applied to a variety of nonelectron transfer organic systems, most recently by Murdoch (45).

III. Atom and Proton Transfers

We describe here some recent developments in light atom transfers for collinear collisions, and then extend the basic idea to actual systems.

In the transfer of an H between two heavy atoms, e. g. ,

$$I + HI \rightarrow IH + I \qquad (8)$$

one expects that the H atom coordinate can be treated as 'fast' and the motion of the I's as 'slow'. (I. e. , one has a Born-Oppenheimer type of approximation.) In the the theory one would solve for the vibrational eigenvalue of the light particle (H), at fixed positions of the heavy particles I and then allow the I's to move in the presence of this effective potential created by the averaged motion of the H. To treat this in a practical way, Babamov and I used polar coordinates (R, θ) in the usual mass-weighted skewed-axes coordinate space (46). The radial coordinate R corresponds approximately to the I-I motion and the angular coordinate θ to the H motion.

Reaction (8) is a symmetric reaction, and was treated by Babamov in terms of symmetric (s) and antisymmetric (a) wavefunctions for the vibrational motion of the H in the presence of the I's (46). Since the H is initially localized on one of the I's, one can

expect that the probability of reaction will depend both on the s- and a- solutions. E. g., when R is large, an H-wavefunction localized near one I is approximately $\psi_s + \psi_a$, and when localized near the other it is approximately $\psi_s - \psi_a$.

The approach of the two I's under the influence of the symmetric state H-motion can be treated quantum mechanically, and similarly for the approach when the H-motion is in an antisymmetric vibrational state. One finds that the reaction probability p for a system in an initial HI vibrational state i to yield a final vibrational state i of the product IH is, approximately, (46)

$$p_{i \leftarrow i} = \sin^2(\eta_a - \eta_s) \tag{9}$$

where η_a (η_s) is the so-called phase shift for the I-I motion when the I's approach under an effective a- (s-) state of the H. By calculating these phase shifts, p was calculated and compared with the exact (many coupled states) quantum mechanical value for p, for the assumed potential energy surface. The results are given in Fig. 1, taken from a paper with Babamov and Lopez (47). The circles denote the exact quantum values (48) and the solid line is that calculated

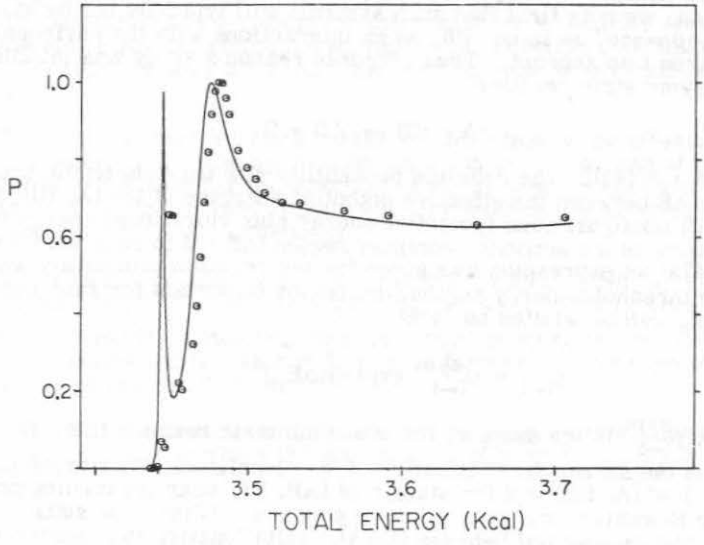

Fig. 1 Reaction probability for reaction (8) when the reactants are in their lowest vibrational state, plotted versus total energy.

from eq (9), when the translational energy of relative motion of the I and HI is varied. Under the conditions investigated, $p_{f\leftarrow i}$ is negligible except for f = i, i. e., when the vibrational quantum number of the HI product equals that of the HI reactant.

The spike in Fig. 1 is due to a "resonance": the effective potential in the s- state of the H- motion forms a well for the I-I motion at smaller I-I distances, due to the delocalization of the H. This well creates a quasi-bound level, i. e., a "resonance" at some energy of the I-I motion and creates the spike. Equation (9) also has an approximate version (46) where

$$\eta_a - \eta_s \cong \gamma e^{-Q_0} \quad , \tag{10}$$

Q_0 being the usual tunneling integral for the H-motion at the distance R_0 of closest approach and γ a known constant. In this approximate form eq. (9) was applied by Bondi et al. to calculate rate constants for collinear collisions, with quite good agreement with exact numerical quantum values (49, 50).

The comparison in Fig. 1 shows that the behavior of the H atom transfer for this system is well understood, both qualitatively and quantitatively. For application to more complex systems, e. g., in solution, we note first that such systems will typically not be exactly "in resonance" as in eq. (9), when interactions with the environment are taken into account. Thus, for this reason a study was initiated of a nonsymmetric reaction

$$A + HB \rightarrow AH + B \tag{11}$$

with $A \neq B$ (47). The reaction probability now depends on the energy defect ΔE between the effective potential energies of the (A, HB) and (AH, B) configurations (potential energy plus vibrational energy of the H motion) in the activated complex region ($\Delta E = 0$ in reaction (9)). In ref. (47a) an expression was given for the reaction probability which, in the threshold energy region (the region important for rate constants), can be written as (47b)

$$p_{f\leftarrow i} = p^{sym}_{f\leftarrow i} \exp[-\beta(\Delta E_{if})^2] \quad , \tag{12}$$

where $p^{sym}_{f\leftarrow i}$ is the same as for the symmetric reaction ($\Delta E = 0$). ΔE_{if} is the ΔE for the ("diabatic", i. e., localized) (47) vibrational state i of (A, HB) and for state f of (AH, B), near the turning point of the R-motion, and β is a known constant. When β is sufficiently large the exponential behaves like the delta function that occurs in electron transfer reactions. ΔE_{if} was assumed small relative to vibrational spacings of E_f.

To apply (12) to an H-transfer in complex systems, we proceed as follows: We classify all coordinates as either fast or slow, the

latter including reaction coordinate. The 'fast' coordinates are taken to be the H being transferred and any other nearby H's, for example any attached to CH_3's, NH_2's, etc. which merely change slightly their equilibrium position or vibration frequencies, as well as any which may simultaneously transfer from one molecule to an adjacent one. Holding all remaining nuclei fixed, the energy defect is now written as $\Delta E_{if}(q)$, where i now denotes the (diabatic) vibrational state of all fast coordinates in the reactants. f is that in the products, and q denotes the totality of all slow coordinates. One of these q's is designated as the reaction coordinate q_R, e. g., the AB distance in reaction (11), and the remaining q's are denoted by q'. The reaction probability depends on the energy defect in the transition state region $\Delta E_{if}(q')$ (namely, at the turning point of the R-motion); the reaction probability also depends on the initial energy along q_R, $E_R(q_R)$, and on the initial state i of the H's. If we denote this reaction probability by $p_{f\leftarrow i}$, the rate constant k is given by (51)

$$k = \sum_i \int \cdots \int p_{f\leftarrow i} p_{iq'}^{eq} \, dq' \, dE_R/h \qquad (13)$$

where $p_{iq'}^{eq}(E_R)\, dq'\, dq_R dp_R/h$ is the equilibrium probability at the given temperature of finding the slow coordinates in the volume element dq', the fast coordinates in a collective quantum state i, and the system in a phase space volume element $dq_R dp_R$ for the reaction coordinate. The integration is over all q' and E_R, and the sum is over all initial states i.

The detailed theory thus includes a calculation of the effective potential energies for the q_R motion, as a function of q, and of using a suitable expression for the reaction probability p. Should any of the q''s in eq. (13) be, instead, high frequency motions, a quantum treatment for their motion can be used.

When there are additional H's as in nearby CH_3's, NH_2's, etc., expression for $p_{f\leftarrow i}^{sym}$ in (47) is modified; Franck-Condon factors for these additional H's could be added as a first approximation. (When there is a concerted transfer of H's, still further modification of (47) is needed, of course.)

Purely to illustrate eqs. (12) and (13) we give a calculation for a very simple model in which the effect of the q''s on E_i and E_f is quadratic:

$$E_i(q') = E_i^0 + \frac{k_r}{2} (q' - q'_{ro})^2 \qquad (14)$$

$$E_f(q') = E_f^0 + \frac{k_p}{2} (q' - q'_{po})^2 \quad . \qquad (15)$$

(For notational brevity we have only used one term; k is actually a square matrix, one $q' - q'_{r0}$ is a column vector and the other a row vector.) In eq. (14) E_i^0 is the value of E_i at some value of q', $q' = q'_{r0}$, etc. If the additional contribution of the q' coordinates to the potential energy is written as $V_r(q')$ in the reactants' configuration, the integral over q' becomes

$$\int e^{-\beta(\Delta E_{if})^2} p_{iq'}^{eq} dq' = \frac{\int e^{-\beta[\Delta E_{if}(q')]^2} e^{-V_r(q')/kT} e^{-E_i(q')/kT} dq'}{\sum_i \int e^{-V_r(q')/kT} e^{-E_i(q')/kT} dq'} \quad (16)$$

where $E_i(q')$ is given as a function of q' by eq. (14). For various models of $V_r(q')$ eq. (16) can be integrated. The presence of the $\beta(\Delta E_{if})^2$ term produces the type of reorganization which appeared in electron transfer reactions (5, 12, 17), when ΔE_{if} depends on q'. If it were independent of q', the right hand side of eq. (16) would become simply $\exp[-\beta(\Delta E_{if})^2]$ and the result would reduce to that in ref. (47).

We plan to implement eq. (13) elsewhere for H and H^+ transfer. We discuss its relation to standard expressions in Sec. IV.

Finally, we comment briefly on a Franck-Condon type calculation for atom transfers. The profile of the potential energy surface vs the coordinate of the H-atom in transit is typically a double well. The latter has sometimes been approximated by two harmonic oscillator potentials, each localized on one of the two wells. Franck-Condon type arguments, e. g., use of eq. (3) involving the overlap of harmonic oscillator vibrational wavefunctions, are then used. However, such a procedure leads to orders of magnitude error in the absolute rates (52, 53). Thus, a different approach is desirable for atom transfers, such as that given in eq. (9) of the present paper for resonant symmetric on-resonance reactions and eq. (12) for asymmetric or off-resonant ones.

IV. Similarities and Differences Between Electron and H-Transfers

The principal similarity of these two types of reactions is the presence of fast and slow coordinates. In an electron transfer reaction the motion of the electrons in the reactants, and that in the surrounding solvent (appearing in the D_{op}) are the fast coordinates. The nuclei are the slow coordinates. In an H atom or H^+ transfer, the fast coordinates are those of all the relevant H's, including the H or H^+'s being transferred and all remaining nearby H or H's. The slow coordinates are the rest of the coordinates (the q's in the previous section).

This theory involving the assumption of both fast and slow coordinates may be compared or contrasted with the conventional approach in transition state theory. Here, it is often (though not always) assumed that all coordinates but the reaction coordinate are the fast coordinates. This approximation is made tacitly when one assumes that at each q_R the averaged motion of the other coordinates yields eigenvalues $E_i(q_R)$, which act as an effective potential for the motion along q_R. Such an approximation implies that all such coordinates are 'fast', relative to the reaction coordinate. One then focuses attention on these energy levels in the transition state region (at $q_R = q_R^{\ddagger}$) and calculates a rate constant. For H-transfers the tunneling integral used is the same as the WKB tunneling integral in Q_0 in eq. (10). What is new is eq. (9), the treatment using coupled H's (nearby H's), the presence of the γ (probably of the order of unity) in eq. (10), and the presence of the $\exp[-\beta(\Delta E_{if})^2]$ in eq. (12). The latter leads, as already noted, to a type of reorganizational term of the environment, neglected in conventional transition state theory. Another treatment of a reorganizational term, based on eq. (3) plus added approximations, rather than on eqs. (12)-(13), has been given by Dogonadze, Kuznetsov and Levich (54).

Equations (9), (10) and (12), when applied via eq. (13), appears to provide a dynamical treatment more detailed and fundamental than existing treatments of H and H^+ transfers. Having said this, one cannot overemphasize the detailed insight which conventional transition state theory has yielded for H and H^+-transfers including, in the electrochemical case, the hydrogen evolution reaction. Equations (9), (10), (12) and (13) are intended to be applied to such reactions.

While electron and H-atom (proton) transfers have much in common, as we have noted above, there are also a number of differences:

(i) The Born-Oppenheimer type separation of variables is more accurate for electron-nuclei systems than for H atom-heavy nuclei systems. Thereby, the reaction probability is not as sharply a peaked function of the energy-defect ΔE in the transition state region. In electron transfer reactions the important role of this energy defect appears, in the case of the all-quantum treatment eq. (3), in the form of the Dirac delta function $\delta(E_f - E_i)$, while in a classical treatment it appears in the assignment of the transition state to the intersection of the reactants' and products' potential energy surfaces. In H transfers it appears in the present paper via an energy defect ΔE, as in eq. (12).

(ii) The H-atom transfer does not entail a charge transfer, and so does not involve the major solvent reorganization which accompanies electron transfer. The H^+-transfer is frequently over a quite short distance (e.g., a transfer between adjacent molecules) and so it, too, is not expected under such conditions to yield a large solvent reorganization energy. Of course, when the proton transfer proceeds via an intervening water molecule $AH^+ \overset{\frown}{O}H_2 \overset{\frown}{B}$ and involves a

concerted motion of the two H^+'s, the effective transfer of charge is over a larger distance, and so would entail a somewhat larger reorganization energy. Such a H_2O bridge removes any need, incidentally, for breaking any pre-existing H-bonds. However, in H^+ transfers involving carbon acids and bases, unlike transfers solely between N's and O's, there may be some preliminary desolvation of the noncarbon acid or base, creating thereby an added barrier to the reaction in the form of a "work term" (55).

(iii) Electron transfers usually involve a weak overlap of the electronic orbitals of the reactions, whereas H atom transfers or H^+ transfers are expected to involve strong overlap. This difference requires a more detailed electronic structure calculation of the potential energy surface in the vicinity of the transition state for H- and H^+-transfers than was necessary for electron transfers.

(iv) In electron transfers there are usually only two electronic states accessible--one for the reactants and one for the products--because of the wide spacing of electronic energy levels. (Reactions at metal electrodes are an exception, because of the many electronic levels in a metal (1, 5). No inverted effect is predicted to occur there, therefore (63). Again, in a homogeneous reaction an excited electronic state of the reaction products may also become accessible.) In the case of H's or H^+'s, however, there are frequently a substantial number of vibrational states of the H's accessible, rather than just two.

(v) In sufficiently exothermic H or H^+ transfer reactions the reaction may be 'downhill' throughout, with no need for H-tunneling (56). A corresponding phenomenon is unlikely for electron transfers, except for 'strong overlap' reactions.

V. Summary

In the present paper we have summarized some recent experiments on electron transfer reactions, recent calculations based on the equations of ref. 5, apart from inclusion of a relatively minor nuclear tunneling factor or an 'electron transfer over a distance' factor. These two factors affect the rate in opposite directions. The calculation of the frequency of solvent fluctuations outside the innermost coordination shell of an ion was described in eq. (6).

We have also described a recent development in the dynamics of H-atom transfers due to Babamov, Lopez and Marcus. We have now outlined how to extend it to H or H^+ transfers in more complicated systems and in condensed media. The treatment is based on a Born-Oppenheimer type separation of fast coordinates (the nearby H's, including the one or two being transferred) and slow coordinates (all other coordinates). Similarities and differences with the theory

of electron transfer are compared in Sec. IV, and both are compared with conventional transition state theory.

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Appendix A. Derivation of Equation (4)

To obtain k_{na}^{max} in eq. (3) we first set the Franck-Condon factor $P_{f \leftarrow i}$ equal to its maximum value of unity. The sum over f is then replaced by an integral over E_f: $\int (df/dE_f)\, dE_f \delta(E_i - E_f)$, where df/dE_f is the density of final states. For a one-coordinate type problem (e. g., a concerted combination of outward symmetric breathing vibration of one reactant with inward breathing vibration of the other in an electron transfer), the density of final vibrational states is $1/\hbar\omega$ where $\hbar\omega$ is the vibrational quantum. Integration then yields eq. (4). Equation (3) assumes, of course, that the density of final states is sufficiently large that it can be treated as a continuum. Typically, the many degrees of freedom provide this continuum, but we have used a pure vibrational model for purposes of deriving eq. (4).

Appendix B. Inner Coordination Shell Contribution to the Energy Barrier

One interesting aspect of the calculations of the innermost coordination shell involves the use of appropriate force constants: If a detailed force constant analysis of the metal-ligand stretching vibrations is made, there are diagonal and off-diagonal bond force constants. Both terms contribute to the differences in the various normal mode metal-ligand stretching frequencies. In calculating the contribution of the innermost shell to the energy barrier, all of these constants are to be included. The calculation is made simpler, when the normal modes remain intact upon electron transfer, by using normal mode force constants (12). They are automatically diagonal but contain both the diagonal and off-diagonal bond force constants as contributing factors. Several recent calculations (57, 58) included only the diagonal bond force constants, as we and others have noted (59). This point of using the normal mode force constants was indeed stressed earlier (5) and used in an early numerical calculation (60). Other treatments used diagonal bond force constants (61). Hush (62) calculated potential energy surfaces for the innermost coordination shell, rather than using known vibration frequencies, and then used the equivalent of a small displacement approximation.

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